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Preparation of oriented and aligned H₂ and HD by stimulated Raman pumping

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Stimulated Raman pumping has been used to prepare oriented and aligned samples of H₂($\nu=1, J=1, 2, 3$) and HD($\nu=1, J=2$) under collision-free conditions using the (1,0) $S(0)$, $S(1)$, $Q(1)$, $Q(2)$, and $O(3)$ lines. The M -sublevel anisotropies were interrogated by polarized [2+1] resonance-enhanced multiphoton ionization via the (0,1) $O(2)$, $O(3)$, and $S(1)$ lines of the $E, F^1\Sigma_g^+ - X^1\Sigma_g^+$ system. The optical excitation schemes employed in this study generate highly oriented and aligned molecular ensembles. We show that the H₂($\nu=1, J=2, M=0$) and H₂($\nu=1, J=2, M=2$) samples retain their initial polarization for greater than 100 ns and are therefore suitable candidates for targets or projectiles in future scattering experiments. © 2008 American Institute of Physics. [DOI: 10.1063/1.2973628]

INTRODUCTION

Molecular hydrogen, having only two electrons, is the simplest neutral diatomic molecule. Controlling the direction of the rotational angular momentum of this molecule proves to be challenging, however, because molecular hydrogen has no permanent dipole moment and the first allowed electronic transitions lie in the vacuum ultraviolet region of the electromagnetic spectrum. Nevertheless, much interest is attached to preparing aligned ($+M$ magnetic sublevels have the same populations as $-M$ sublevels, but the populations differ among $|M|$ values) or oriented ($+M$ magnetic sublevels have a different population than $-M$ sublevels) samples of H₂, HD, or D₂ either for studying the behavior of such isolated molecules or for using them as targets or projectiles in scattering experiments. Please note that oriented molecules have typically some degree of alignment as well. Alignment and orientation refer here to the distribution of rotational angular momentum vectors \mathbf{J} . In the high- \mathbf{J} limit the results become classical and the plane of rotation of the molecule is perpendicular to \mathbf{J} .

One approach to preparing aligned or oriented samples is the use of optical fields that interact with the molecules. Circularly polarized light can prepare oriented and aligned samples, whereas linearly polarized light can prepare only aligned samples. A particular example is stimulated Raman pumping (SRP), in which the energy difference of two photons is tuned to correspond to a particular rovibrational transition in the molecule.

Several groups have reported the use of SRP to prepare aligned molecules. Among the first were Sitz and Farrow,¹ who prepared an aligned sample of room-temperature N₂($\nu=1, J=0-14$) and measured subsequent collision-induced decay of the alignment. Rudert *et al.* extended this approach to polyatomics and reported the preparation of aligned samples of acetylene.² The preparation of rovibrationally excited but unaligned samples of molecular hydrogen using SRP was performed as early as 1983 by Brodnikovskii *et al.*³ In 1988 Farrow and Chandler⁴ reported the measurement of rotational energy transfer rates of H₂($\nu=1$, low J) prepared in this manner. An aligned sample of hydrogen deuteride was prepared by SRP to investigate the effects of alignment on the reactivity for the Cl+HD($\nu=1, J=2$) hydrogen abstraction reaction by Kandel *et al.*⁵ The first report of the preparation of aligned H₂($\nu=1, J=1$) was by Cureton-Chinn *et al.*,⁶ which was done at atmospheric pressure and room temperature. Isakson⁷ has prepared and characterized an aligned sample of H₂($\nu=1, J=3$) under collision-free conditions.

In the present work we go beyond these previous studies and present, to our knowledge, the first report of the preparation of *oriented* H₂($\nu=1, J=2, 3$) and aligned HD($\nu=1, J=2$) under collision-free conditions using SRP, where [2+1] resonance enhanced multiphoton ionization (REMPI) has been used to measure the degree of orientation or alignment of the samples. Significantly, we demonstrate that the prepared polarization anisotropy of the H₂ and HD samples does not degrade on time scales relevant for their use as reagents in scattering experiments. Although the present study concerns the orientation and alignment of molecular hydrogen and its isotopomers, the procedure we present is believed by us to be generally applicable.

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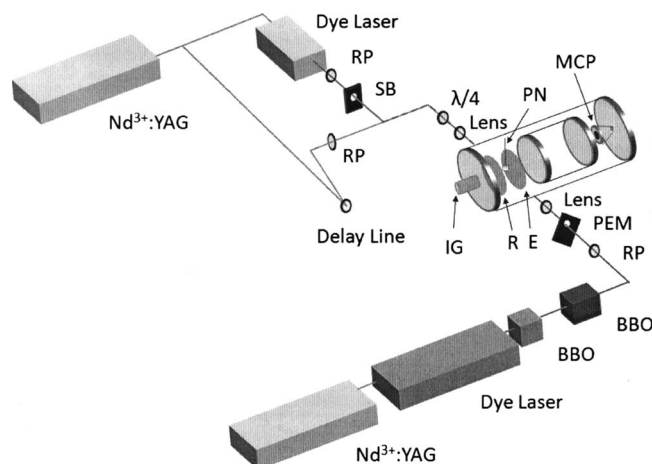


FIG. 1. Schematic diagram of experimental apparatus. Abbreviations are as follows: BBO= β -barium borate crystal; E=extractor grid; IG=(nude) ion gauge; MCP=microchannel plates; PEM=photoelastic modulator; PN=pulsed nozzle; R=repeller plate; RP=Rochon prism (linear polarizer); and SB=Soleil Babinet compensator (variable waveplate). The $\lambda/4$ waveplate is used for orientation but removed for alignment preparation.

EXPERIMENTAL METHODS

In this section the techniques pertaining only to the present study are given as the experimental apparatus has been described in detail elsewhere.^{8,9} In brief, a mixture of 10% H_2 (Praxair 99.995% purity) or HD (Cambridge Isotopes 97% purity) in Ar was expanded supersonically into a vacuum chamber through a solenoid-driven pulsed valve, producing almost exclusively $H_2(\nu=0)$ or $HD(\nu=0)$ in low rotational levels. Subsequently, the H_2 or HD were excited to the $\nu=1$ vibrational state by means of SRP transitions; in the present study, the $S(0)$, $S(1)$, $Q(1)$, $Q(2)$, and $O(3)$ transitions were employed. For example, the $H_2(\nu=1, J=2, M=0)$ and $H_2(\nu=1, J=2, M=2)$ states were, respectively, produced by pumping with linearly and circularly polarized light tuned to the $S(0)$ line. Following a variable time delay, the excited-state H_2 or HD molecules were detected state-specifically by $[2+1]$ REMPI via the $O(2)$, $O(3)$, and $S(1)$ lines of the $E, F^1\Sigma_g^+ - X^1\Sigma_g^+(0,1)$ band; the polarization of the REMPI probe beam was the same as that used for pumping. The H_2^+ or HD^+ ions were then collected by a time-of-flight (TOF) mass spectrometer and detected on a pair of microchannel plates. Figure 1 shows the experimental setup, and Table I summarizes the SRP and $[2+1]$ REMPI wavelengths relevant to this study.

TABLE I. Summary of the SRP and $[2+1]$ REMPI transitions used in this study, along with their associated wavelengths. The wavelengths listed for SRP refer to the Stokes beam, while the pump beam is always at 532 nm.

Transition	H_2/HD SRP (nm)	H_2/HD [2+1] REMPI (nm)
$O(2)$...	211.243/209.572
$O(3)$	656.263/640.296	211.856/210.030
$Q(1)$	682.847/659.145	...
$Q(2)$	682.276/658.800	...
$S(0)$	699.258/670.640	...
$S(1)$	710.128/678.223	209.899/208.571

The pump and Stokes wavelengths necessary for SRP were produced using the second harmonic of an injection-seeded Nd^{3+} :YAG (yttrium aluminum garnet) laser (Continuum PL9020) and the output of a dye laser (Continuum ND6000, LDS698 dye), respectively. A delay line was used to achieve a temporal overlap of the beams before their combination and subsequent focusing into the chamber by an $f=60$ cm lens.

A linear polarizer was placed at the beginning of each beamline to remove unwanted polarization components from the Nd^{3+} :YAG and dye laser outputs. While alignment studies may be carried out with linearly polarized pump and Stokes beams, orientation studies require that the pump and Stokes beam have circular polarizations of opposite helicity.¹⁰ In the SRP process, one photon of the pump beam is absorbed while one photon is emitted into the Stokes beam; therefore, beams with opposite helicity lead to $\Delta M = \pm 2$ transitions. Circular polarization of the pump beam, which has a fixed wavelength of 532 nm, was achieved using a zeroth-order $\lambda/4$ waveplate (antireflection coated for 532 nm) placed immediately before the entrance of the chamber. However, in addition to polarizing the pump beam at 532 nm, this waveplate induces some shift in the phase of the Stokes beam. To ensure that the Stokes and pump beams have opposite helicity, we placed a Soleil Babinet compensator in the Stokes beamline to correct for the phase-shift induced by the 532 nm waveplate and to give the Stokes beam the correct overall circular polarization. The quality of the polarizations of both the pump and Stokes beams was analyzed after the exit window of the chamber using a Fresnel rhomb, followed by a linear polarizer.¹¹

Our setup described above has two principal advantages. First, we are able to control the polarizations of the pump and Stokes beams independently. Second, with the Soleil Babinet compensator we are able to preserve the helicity of the Stokes beam while tuning it over a wide range of wavelengths. This flexibility is important for the goals of our future experiments, as H_2 , HD, and D_2 have several SRP transitions of interest ranging from about 600 to 800 nm. By way of contrast, while it is possible to prepare pump and Stokes beams with opposite helicity using a single custom-made waveplate,⁶ the effective wavelength range of such an optic is much narrower, and the purity of polarization becomes increasingly degraded as wavelengths are tuned away from the design of the optic.

The pump and Stokes wavelengths were initially matched to an SRP transition by monitoring the coherent anti-Stokes Raman spectroscopy (CARS) signal emerging from a cell, filled with ~ 2 Torr H_2 , placed in the beam path. The CARS signal was isolated from the pump and Stokes beams using a series of optical filters; the signal can be seen by eye when the wavelength difference between the pump and Stokes beams is close to the line center of the transition. It may be useful to point out that the pump and Stokes beams are not brought to a tight focus, so that relatively large volumes of target molecules can be oriented or aligned by this procedure.

The probe light for the ionization of the H_2 or HD was generated by frequency tripling the output of another

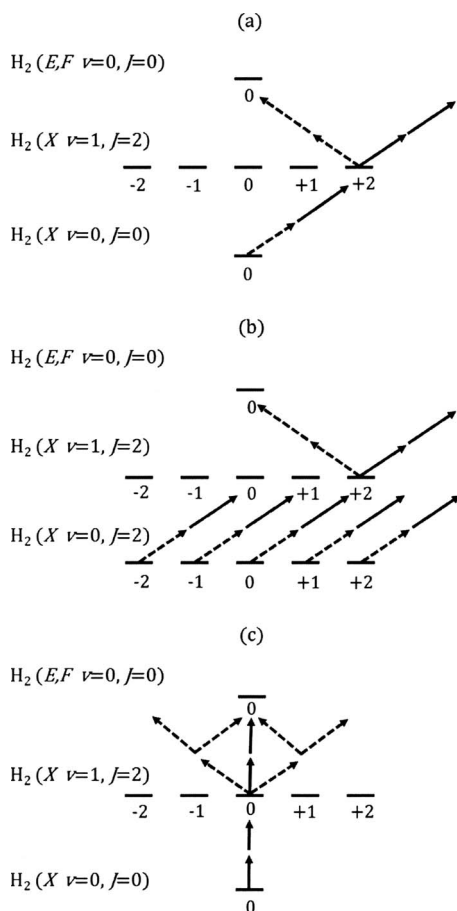


FIG. 2. SRP Pumping/REMPI detection schemes shown for (a) $S(0)$ circular/ $O(2)$ circular, (b) $Q(2)$ circular/ $O(2)$ circular, and (c) $S(0)$ linear/ $O(2)$ linear polarizations. In (a) and (b) dashed arrows correspond to LCP SRP and REMPI light, while solid arrows correspond to RCP SRP and REMPI light. In (c) arrows of the same shading (solid or dashed) are used when the SRP and REMPI light polarizations are parallel, and different shading when the polarizations are perpendicular. Note that the two SRP beams co-propagate, whereas the REMPI beam counter-propagates with respect to the SRP beams.

Nd³⁺:YAG-pumped dye laser (Lambda Physik LPD3000, DCM dye) using two BBO crystals in sequence to produce approximately 211 nm light. We typically obtain frequency-tripled powers of 0.5–0.8 mJ pulse⁻¹, but much of this power is dissipated by optics in the beamline, with the result that only about one-third of the initial power actually reaches the ionization region. The frequency-tripled beam passes through a Rochon prism polarizer, which removes unwanted polarization components. The beam subsequently passes through a photoelastic modulator (PEM) (Hinds PEM-80), which acts as a $\lambda/2$ wave plate on an every-other-shot basis. For orientation experiments requiring circularly polarized light, a 213 nm zeroth-order $\lambda/4$ waveplate was placed in the beamline after the PEM. In this fashion we are able to alternate the REMPI probe beam between left-circular polarization (LCP) and right-circular polarization (RCP) with respect to the fixed polarization of the SRP beams on an every-other-shot basis. Finally, the probe beam was focused into the center of the TOF chamber using an $f=50$ cm lens, at which point it intersects the two SRP beams and the molecular beam. It should be noted that because the SRP and REMPI

beams are counterpropagating, the two sets of beams give two different laboratory frames related by a 180° rotation. As far as the molecules are concerned what is LCP in one propagation direction would be RCP in the opposite propagation direction. Thus, for example, an $M=+2$ state in the frame of the SRP laser beams would be detected by counter-propagating LCP light; LCP photons have a positive angular momentum projection along the direction of propagation.¹¹ In our experiment, the SRP laser beams create the orientation or alignment of the molecules, and therefore these beams define the Z axis of our laboratory frame.

The REMPI lines were first identified by flowing room-temperature H₂ or HD over a hot, nude ion gauge through a variable leak valve (Varian model 951-5106), which produces H₂ or HD in ($\nu=1, J<10$) states. We are able to distinguish Q -branch lines from O - and S -branch lines as the former have drastically weaker line strengths when circularly polarized light is used.^{12,13} In Fig. 2 we show the pumping and detection schemes for the two types of laser polarizations.

RESULTS AND DISCUSSION

Orientation of H₂($\nu=1, J=2$)

Figure 3 displays the measured signals I_L and I_R for the detection of H₂($\nu=1, J=2, M=+2$), as prepared with the SRP $S(0)$ line and detected with the REMPI $O(2)$ line, for a 20 ns pump-probe time delay. Here, I_L and I_R refer to H₂⁺ ion signal with LCP or RCP probe light, respectively. It should be noted that no hyperfine depolarization of the sample is expected as we are preparing a state with even rotational quantum number J , for which the total nuclear spin $I=0$. The intensities for these signals can be expressed in terms of a multipole expansion¹⁴

$$I = I_0 [1 + s_1 A_0^{(1)} P_1(\cos \theta) + s_2 A_0^{(2)} P_2(\cos \theta) + s_3 A_0^{(3)} P_3(\cos \theta) + s_4 A_0^{(4)} P_4(\cos \theta)], \quad (1)$$

where $A_0^{(k)}$ are the time-independent moments of the multipole expansion of the angular momentum distribution, and s_k are the REMPI sensitivity factors for the $A_0^{(k)}$ using this detection scheme.^{15–17} The s_k change sign with the helicity of the circularly polarized REMPI beam only for odd k .¹¹ The

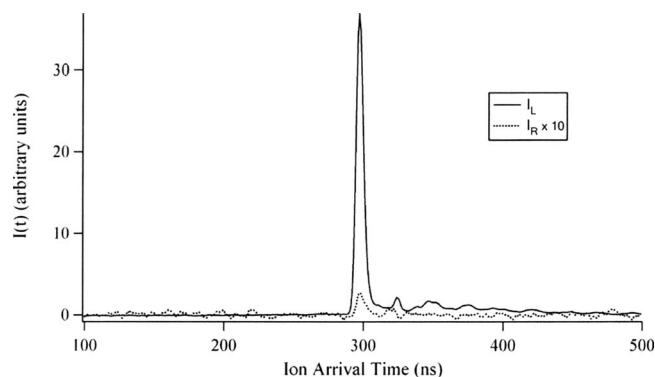


FIG. 3. Ion signals for left- and right-circularly polarized light used in the detection of H₂($\nu=1, J=2, M=2$). The data shown were taken using a pump-probe time delay of 20 ns. The I_R signal has been multiplied by a factor of 10.

$P_k(\cos \theta)$ are k th order Legendre polynomials, where θ is the angle between the major axes (+Z) of the laboratory frame (defined by the propagation direction of the SRP beams for circular polarization) and the probe laser frame (defined by the propagation direction of the REMPI beam for circular polarization). In the present case the beams are counter-propagating, so that $\cos \theta = -1$. From Eq. (1), we obtain

$$I_L = I_0[1 + |s_1|A_0^{(1)} + |s_2|A_0^{(2)} + |s_3|A_0^{(3)} + |s_4|A_0^{(4)}], \quad (2)$$

$$I_R = I_0[1 - |s_1|A_0^{(1)} + |s_2|A_0^{(2)} - |s_3|A_0^{(3)} + |s_4|A_0^{(4)}]. \quad (3)$$

For the $O(2)$ line of the $E, F^1\Sigma_g^+ - X^1\Sigma_g^+$ transition using circularly polarized light and assuming 100% population in the $M=2$ state, $s_1 = |s_1| = \sqrt{6}$, $s_2 = 10/7$, $s_3 = |s_3| = \sqrt{6}$, $s_4 = 12/7$, $A_0^{(1)} = \sqrt{2/3}$, $A_0^{(2)} = 1$, $A_0^{(3)} = 1/2\sqrt{6}$, and $A_0^{(4)} = 1/24$. The signal I_R is predicted to vanish, which can be seen by inserting these values into Eqs. (2) and (3). The same result is also reached by examination of the scheme shown in Fig. 2(a). Experimentally, however, we expect to observe nonzero I_R signals because imperfections in the purity of the circularly polarized light in both the SRP and REMPI beams allow for population and detection of states other than the $M=2$ sublevel.

Recall that the $H_2(\nu=1, J=2)$ level does not undergo hyperfine depolarization (as the total nuclear spin $I=0$): therefore, a study of the ratio I_L/I_R versus pump-probe time delay indicates the extent of collisional depolarization of the sample. The ratio I_L/I_R is determined by integrating over the measured signals. We recorded I_L/I_R for pump-probe delays between 0 and 100 ns and the results are presented in Fig. 4. The results demonstrate that the initial orientation is retained on time scales relevant for studying isolated chemical reactions. Under optimal experimental conditions, namely, if the polarizations of the pump and probe beams are almost completely pure, we have seen I_L/I_R ratios in excess of 100:1 (Fig. 3), which indicates that the probed sample is almost entirely in the $M=2$ sublevel.

Oriented $H_2(\nu=1, J=2)$ samples were also prepared using circularly polarized light with the SRP $Q(2)$ line, which theoretically is expected to populate the $M=0, 1$, and 2 sublevels in a 2:3:2 ratio. However, because this sample was probed with circularly polarized light tuned to the $O(2)$ REMPI transition, the I_R signal is again predicted to vanish, as shown in Fig. 2(b). In this case, we observed an $\sim 10:1$ I_L/I_R ratio. Again, we attribute a nonzero I_R signal to imperfections in the laser polarizations but we note also that Q -branch SRP line strengths for linearly polarized light are substantially larger than the corresponding S - and O -branch SRP lines (see additional discussion below). We therefore believe that impurities in the SRP polarizations lead to significant population of all M sublevels and, in particular, $M=-2$, which accounts for the reduced I_L/I_R ratio. Based on the results presented in Fig. 4, we expect an oriented sample of $H_2(\nu=1, J=2)$ to also be preserved for long times.

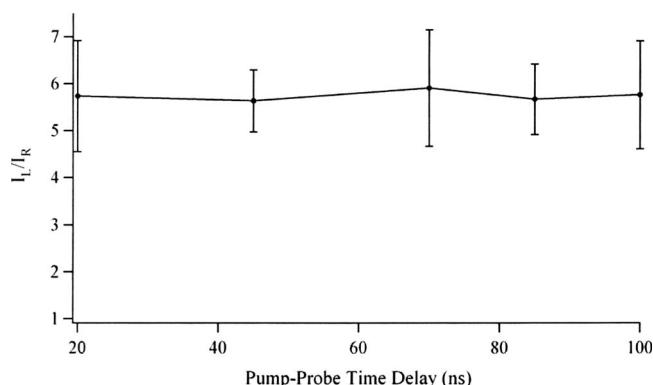


FIG. 4. The ratio of integrated I_L/I_R signals as a function of pump-probe time-delay shown for the detection of $H_2(\nu=1, J=2, M=2)$. The error bars are calculated as 2σ from three measurements at each time delay.

Alignment of $H_2(\nu=1, J=2)$

We measured the degree of alignment of the $H_2(\nu=1, J=2, M=0)$ sublevel, as prepared with the SRP $S(0)$ and detected by REMPI $O(2)$ transitions, using linear polarizations in each beamline. Because linearly polarized light is insensitive to odd moments of the angular momentum distribution, the intensities are given by

$$I_{\parallel} = I_0[1 + s_2A_0^{(2)}P_2(1) + s_4A_0^{(4)}P_4(1)] \\ = I_0[1 + s_2A_0^{(2)} + s_4A_0^{(4)}], \quad (4)$$

$$I_{\perp} = I_0[1 + s_2A_0^{(2)}P_2(0) + s_4A_0^{(4)}P_4(0)] \\ = I_0[1 - \frac{1}{2}s_2A_0^{(2)} + \frac{3}{8}s_4A_0^{(4)}], \quad (5)$$

where the s_k and $A_0^{(k)}$ have the same meaning as before; but the values of the s_k and $A_0^{(k)}$ are different for linearly polarized light. Their values are $s_2 = -10/7$, $s_4 = 72/7$ (linearly polarized REMPI), and $A_0^{(2)} = -1$, and $A_0^{(4)} = \frac{1}{4}$ (linearly polarized SRP), where we have again assumed that 100% of the population resides in the $M=0$ sublevel in the calculation of $A_0^{(k)}$. Note that for linearly polarized light the frame is defined by the axis of the linear polarization of the electric field, and the SRP polarization defines the laboratory axis ($\theta=0^\circ$). Here I_{\parallel} and I_{\perp} denote, respectively, ion signals for parallel ($\theta=0^\circ$) and perpendicular ($\theta=90^\circ$) directions of the probe laser electric field with respect to the SRP beams. The ratio I_{\parallel}/I_{\perp} , which is also denoted by $I(0)/I(90)$, is expected to be 4:1 for all pump-probe time delays when no depolarization mechanisms are operative. As a proof-of-principle experiment and to investigate the extent of collisional depolarization on the aligned sample, we recorded I_{\parallel} and I_{\perp} for pump-probe delays between 0 and 8 μ s. Figure 5 presents the ratio I_{\parallel}/I_{\perp} versus pump-probe time delay. The results indicate that a sample of $H_2(\nu=1, J=2, M=0)$ has been successfully produced and that the initial alignment is retained to a high degree (there may be evidence for a very small amount of depolarization by 4 μ s) for the entire time span of the experiment. In a similar fashion, we successfully prepared the $HD(\nu=1, J=2, M=0)$ sublevels. Ion-signal ratios consistent with those of the H_2 studies were observed. The ability to prepare and detect H_2 and HD state-specifically using long pump-probe time delays has led us to study the hyperfine depolarization

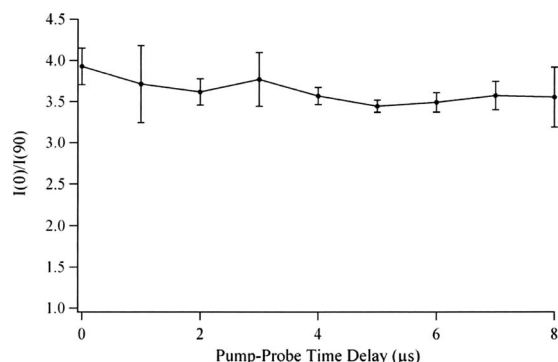


FIG. 5. The ratio of integrated I_{\parallel}/I_{∞} signals as a function of pump-probe time-delay shown for the detection of $\text{H}_2(\nu=1, J=2, M=0)$. The error bars are calculated as 2σ from three measurements at each time delay.

of $\text{HD}(\nu=1, J=2, M=0)$, and these results will be presented in detail elsewhere.¹⁸ In this regard, it might be useful to point out that previous studies have reported the calculated time dependence of the nuclear spin induced depolarization of $\text{H}_2(\nu=0)$ and $\text{D}_2(\nu=0)$ for different rotational levels.¹⁹

Orientation of $\text{H}_2(\nu=1, J=1, 3)$

In addition to the above experiments, we produced highly oriented $\text{H}_2(\nu=1, J=3)$ using the $S(1)$ SRP transition with circularly polarized light, which prepares the $M=3, 2$, and 1 sublevels with population ratios of 15:5:1, whereas all other M sublevels are unpopulated; for detection using the $O(3)$ line, I_L/I_R signal ratios in excess of 100:1 were observed. These ratios correspond to measurements taken with a SRP-probe delay time of approximately 20 ns; a very short delay time was chosen as these states undergo hyperfine depolarization.

Attempts were also made to prepare and detect oriented $\text{H}_2(\nu=1, J=1)$ molecules by pumping with either the $Q(1)$ or $O(3)$ SRP transitions using circularly polarized light and detecting with the $S(1)$ REMPI line, also with circularly polarized light. However, in both cases, we observed a much smaller than expected degree of orientation. We speculate that we are only partially saturating the $[2+1]$ REMPI process due to lower probe powers at this wavelength (209.899 nm). The effect of this is that the ionization step becomes increasingly sensitive to the orientation and alignment of the $E, F(\nu=0, J=1)$ level created by the resonant two-photon REMPI excitation process rather than the orientation of the $X(\nu=1, J=1)$ level that we are attempting to measure. Because it is difficult to measure the degree of saturation, we are unable to present conclusive evidence to support this. Similar effects have been observed for other S -branch REMPI lines, where the magnitude of the alignment was observed to be smaller than expected,⁷ which seems to support our interpretation of the small alignment effect observed for the $S(1)$ transition. By contrast, the $O(2)$ REMPI transition used here produces only $E, F(J=0, M=0)$ in the resonant two-photon step [see Fig. 2(c)]: this level can only be populated but not oriented or aligned, and thus there can be no effects from the inability to saturate the ionization step.

CONCLUSIONS

We have demonstrated that aligned and oriented samples of $\text{H}_2(\nu=1, J=2, 3)$ and $\text{HD}(\nu=1, J=2)$ can be produced via SRP under collision-free conditions. We have also shown that O -branch and S -branch lines of the two-photon $E, F^1\Sigma_g^+ - X^1\Sigma_g^+$ transition are sufficiently sensitive to observe the rotational anisotropy of polarized samples of H_2 and HD .

The $\text{H}_2(\nu=1, J=2)$ state is a natural candidate for use in scattering experiments as this state is not subject to hyperfine depolarization. However, it could be very difficult to undertake these experiments using polarization-sensitive O - or S -branch REMPI detection schemes because these transitions have exceedingly weak line strengths. On the other hand, while the Q -branch line strengths are very large in comparison, the sensitivity of these transitions to rotational polarization, as quantified by the sensitivity factors s_k , is much smaller. To illustrate, we calculated the ratios of the sensitivity factors for the O - and S -branch transitions to those of the Q -branch transition for the detection of $\text{H}_2(\nu=1, J=2)$ using linearly polarized light tuned to an $E, F^1\Sigma_g^+ - X^1\Sigma_g^+$ REMPI transition. If the $Q(2)$ line is used, the sensitivity factors are $s_2 = -0.1133$ and $s_4 = 0.0067$. We see that the corresponding O - and S -branch transitions provide much greater sensitivity to the rotational polarization by calculating the aforementioned ratios: $s_2(O)/s_2(Q) = 12.64$, $s_4(O)/s_4(Q) = 1535$, and $s_2(S)/s_2(Q) = 3.612$, $s_4(S)/s_4(Q) = 12.18$. For the H_2 molecule and its isotopomers, the O - and S -branch line sensitivity factors for the $E, F - X$ system are typically larger by an order of magnitude or more than those for the Q -branch lines.²⁰ Q -branch lines are consequently of little utility for angular momentum polarization studies, although they have already proven to be useful for measuring rotational-state population distributions.^{20–25}

It remains as a challenge whether or not the two-photon $E, F - X$ band system can be used to detect polarized molecular hydrogen produced in chemical reactions under single-collision conditions. The present study does demonstrate that we have a practical means of producing oriented and aligned molecular hydrogen for subsequent studies.

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